

10/007 861
Feb 20 2004



**Europäisches
Patentamt**

**European
Patent Office**

**Office européen
des brevets**

Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

99850160.5

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

DEN HAAG, DEN
THE HAGUE, 28/04/00
LA HAYE, LE



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.: 99850160.5
Demande n°:

Anmeldetag:
Date of filing: 29/10/99
Date de dépôt:

Anmelder:
Applicant(s):
Demandeur(s):
AKZO NOBEL N.V.
6800 SB Arnhem
NETHERLANDS

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:
Silica-based sols

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat:
State:
Pays:

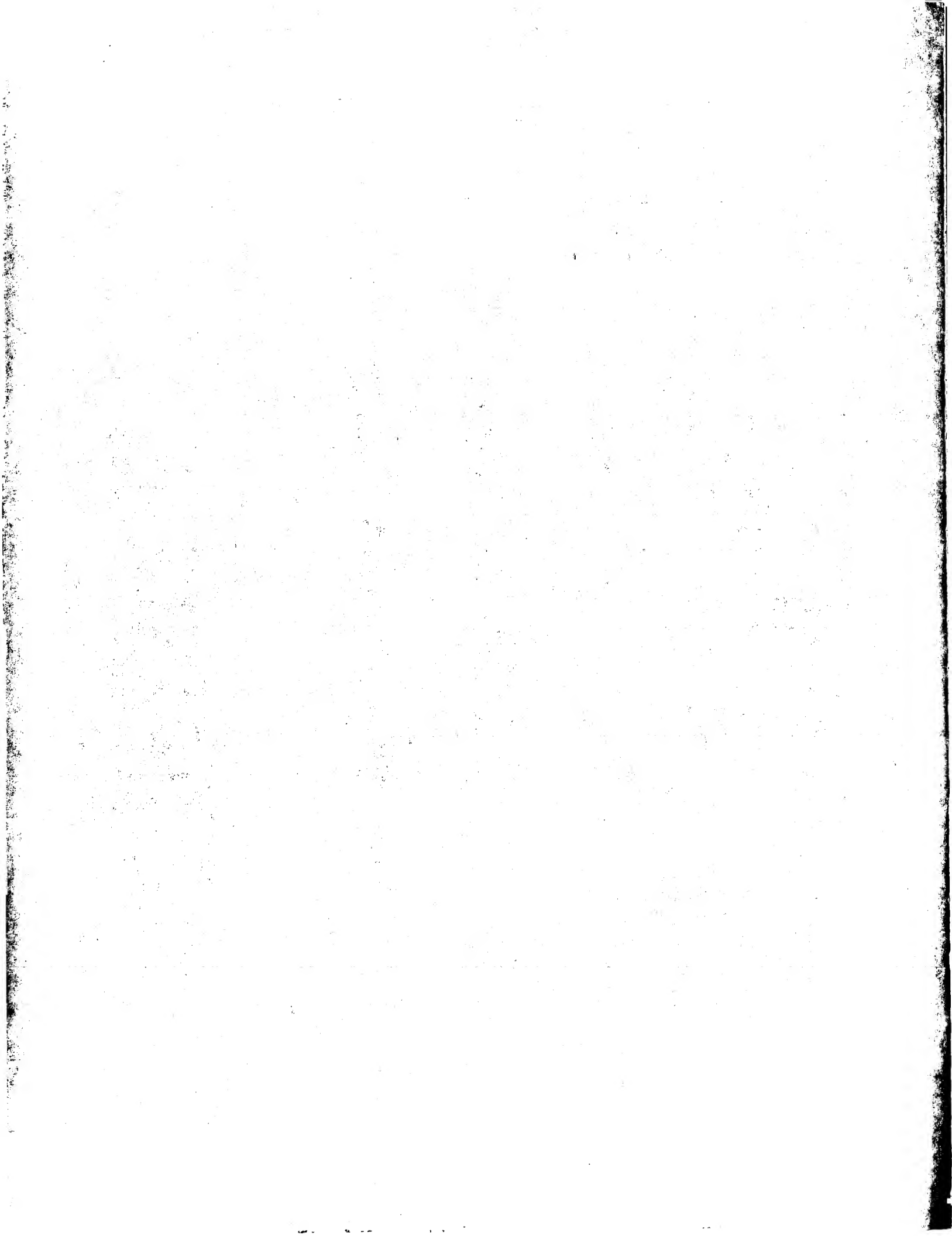
Tag:
Date:
Date:

Aktenzeichen:
File no.
Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:
C01B33/143, D21H17/68

Am Anmeldetag benannte Vertragstaaten:
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE
Etats contractants désignés lors du dépôt:

Bemerkungen:
Remarks:
Remarques:



Silica-based sols

The present invention generally relates to silica-based sols suitable for use in papermaking. More particularly, the invention relates to silica-based sols, a process for the production of silica-based sols, silica-based sols obtainable by the process and a process for the production of paper in which silica-based sols are used as additives. The invention provides silica-based sols with high solids contents, high stability as well as high drainage and retention performance in papermaking.

Background

In the papermaking art, an aqueous suspension containing cellulosic fibres, and optional fillers and additives, referred to as stock, is fed into a headbox which ejects the stock onto a forming wire. Water is drained from the stock through the forming wire so that a wet web of paper is formed on the wire, and the paper web is further dewatered and dried in the drying section of the paper machine. Drainage and retention aids are conventionally introduced into the stock in order to facilitate drainage and to increase adsorption of fine particles onto the cellulosic fibres so that they are retained with the fibres on the wire.

Silica-based particles are widely used as drainage and retention aids in combination with charged organic polymers like anionic and cationic acrylamide-based polymers and cationic and amphoteric starches. Such additive systems are disclosed in U.S. Patent Nos. 4,388,150; 4,961,825; 4,980,025; 5,368,833; 5,603,805; 5,607,552; and 5,858,174; and International Patent Application WO 97/18351. These systems are among the most efficient drainage and retention aids now in use.

Silica-based particles suitable for use as drainage and retention aids are normally supplied in the form of aqueous colloidal dispersions, so-called sols. Commercially used silica-based sols usually have a silica content of about 7-15% by weight and contain particles with a specific surface area of at least 300 m²/g. Sols of silica-based particles with higher specific surface areas are usually more dilute to improve storage stability and avoid gel formation.

It would be advantageous to be able to provide silica-based sols with further improved drainage and retention performance and even better stability. It would also be advantageous to be able to provide a process for preparing silica-based sols with improved drainage, retention and stability properties. It would also be advantageous to be able to provide a papermaking process with improved drainage and/or retention.

The Invention

In accordance with the present invention there is provided silica-based sols which are suitable for use as flocculating agents in water purification and as drainage and

retention aids in papermaking. The silica-based sols according to the invention exhibit good stability over extended periods of time, notably high surface area stability and high stability towards gelation, and hence they can be prepared and shipped at high specific surface areas and high silica concentrations. The sols have improved capability to maintain the high specific surface area on storage at high silica concentrations. The silica-based sols further result in very good or improved drainage and retention when used in conjunction with anionic, cationic and/or amphoteric organic polymers. Hereby the sols of the present invention makes it possible to increase the speed of the paper machine and to use a lower dosage of additives to give a corresponding drainage and/or retention effect, thereby leading to an improved papermaking process and economic benefits. The invention thus relates to silica-based sols as further defined in the appended claims.

In addition to silica-based sols the present invention also relates to a process for the production of silica-based sols and to the use of the sols, as further defined in the appended claims. The preferred field of use for the silica-based sols, in combination with organic polymers as described herein, is as drainage and retention aids in papermaking. The term "drainage and retention aids", as used herein, refers to two or more components (aids, agents or additives) which, when being added to a stock, give better drainage and/or retention than is obtained when not adding the components. The present invention further relates to a process for the production of paper from an aqueous suspension containing cellulosic fibres, and optional fillers, which comprises adding to the suspension a silica-based sol and at least one charged organic polymer, forming and draining the suspension on a wire. The invention thus relates to a process as further defined in the appended claims.

The silica-based sols according to the present invention are aqueous sols that contain anionic silica-based particles, i.e. particles based on silica (SiO_2) or silicic acid. The particles are preferably colloidal, i.e., in the colloidal range of particle size. The silica-based particles present in the sol suitably have an average particle size below about 10 nm and preferably in the range of from about 10 to about 2 nm. As conventional in the chemistry of colloidal particles based on silica, particle size refers to the average size of the primary particles, which may be aggregated or non-aggregated.

The specific surface area of the aqueous silica-based sols is suitably at least 80 m^2/g aqueous sol, i.e., based on the weight of aqueous sol, preferably at least 85 m^2/g aqueous sol, more preferably at least 90 m^2/g aqueous sol and most preferably at least 95 m^2/g aqueous sol. In a preferred embodiment of this invention, the specific surface area of the aqueous silica-based sols is suitably at least 115 m^2/g aqueous sol. Generally, the

specific surface area of the aqueous sol can be up to about 200 m²/g aqueous sol, suitably up to 150 m²/g aqueous sol, preferably up to 130 m²/g aqueous sol and most preferably up to 120 m²/g aqueous sol.

The specific surface area of the silica-based particles is suitably at least 300 m²/g SiO₂, i.e. based on the weight of SiO₂, preferably at least 400 m²/g SiO₂ and most preferably at least 550 m²/g SiO₂. Generally, the specific surface area of the particles can be up to about 1200 m²/g SiO₂, suitably less than 1000 m²/g SiO₂ and preferably up to 950 m²/g SiO₂. In a preferred embodiment of this invention, the specific surface area of the particles is within the range of from 550 to 725 m²/g SiO₂, preferably from 575 to 700 m²/g SiO₂. In another preferred embodiment of this invention, the specific surface area of the particles is within the range of from 775 to 1200 m²/g SiO₂, preferably from 800 to less than 1000 m²/g SiO₂.

The specific surface area can be measured by means of titration with NaOH in known manner, e.g. as described by Sears in Analytical Chemistry 28(1956):12, 1981-1983 and in U.S. Patent No. 5,176,891, after appropriate removal of or adjustment for any compounds present in the sample that may disturb the titration like aluminium and boron species. When expressed in square meters per gram of aqueous sol, the specific surface area represents the specific surface area that is available per gram of aqueous silica-based sol. When expressed in square meters per gram of silica, the specific surface area represents the average specific surface area of the silica-based particles present in the sol.

The silica-based sols have an S-value within the range of from 10 to 45%, suitably from 20 to 40% and preferably from 25 to 35%. The S-value can be measured and calculated as described by Iler & Dalton in J. Phys. Chem. 60(1956), 955-957. The S-value indicates the degree of aggregate or microgel formation and a lower S-value is indicative of a higher degree of aggregation.

The silica-based sols have a molar ratio of SiO₂ to M₂O, where M is alkali metal ion (e.g. Li, Na, K) and/or ammonium, of at least 10:1, suitably at least 12:1 and preferably at least 15:1. The molar ratio of SiO₂ to M₂O generally can be up to 100:1, suitably up to 40:1 and preferably up to 30:1. Preferred ranges are thus from 10:1 to 100:1 and notably from 15:1 to 30:1. The silica-based sols usually have a pH of at least 8.0, suitably at least 10.0, preferably at least 10.5, and more preferably at least 10.6. The pH can be up to about 11.5, suitably up to 11.0.

The silica-based sols should suitably have a silica content of at least 3% by weight but it is more suitable that the silica content is within the range of from 10 to 30% by weight and preferably from 12 to 25% by weight. In order to simplify shipping and reduce transportation costs, it is generally preferable to ship high concentration silica-

based sols but it is of course possible and usually preferable to dilute the sols to substantially lower silica contents prior to use, for example to silica contents within the range of from 0.05 to 5 % by weight, in order to improve mixing with the furnish components. The viscosity of the silica-based sols can vary depending on, for example, the silica content of the sol. Usually, the viscosity is at least 5 cP, normally within the range of from 5 to 40 cP, suitably from 6 to 30 cP and preferably from 7 to 25 cP. The viscosity, which is suitably measured on sols having a silica content of at least 10% by weight, can be measured by means of known technique, for example using a Brookfield LVDV II+ viscosimeter.

10 The silica-based sols of this invention are preferably stable. The term "stable silica-based sol", as used herein, refers to silica-based sols which when subjected to storage or ageing for one month at 20°C in dark and non-agitated conditions exhibit an increase in viscosity of less than 100 cP. Suitably the viscosity increase, if any, is less than 50 cP and preferably less than 30 cP when the sols are subjected to the above
15 conditions.

In a preferred embodiment of this invention, the silica-based sol is substantially free from aluminium. In another preferred embodiment of this invention, the silica-based sol is substantially free from boron. In yet another preferred embodiment of this invention, the silica-based sols are modified using various elements, e.g. aluminium and/or boron, which can be present in the aqueous phase and/or in the silica-based particles. If
20 aluminium is used, the sols can have a molar ratio of Al_2O_3 to SiO_2 within the range of from 1:4 to 1:1500, suitably from 1:8 to 1:1000 and preferably from 1:15 to 1:500. If boron is used, the sols can have a molar ratio of B to SiO_2 within the range of from 1:4 to 1:1500, suitably from 1:8 to 1:1000 and preferably from 1:15 to 1:500. If both aluminium and boron
25 are used, the molar ratio of Al to B can be within the range of from 100:1 to 1:100, suitably from 50:1 to 1:50.

The aqueous silica-based sols according to the invention can be produced starting from a conventional aqueous silicate solution like alkali water glass, e.g. potassium or sodium water glass, preferably sodium water glass. The molar ratio of SiO_2
30 to M_2O , where M is alkali metal, e.g. sodium, potassium, ammonium, or a mixture thereof, in the silicate solution or water glass is suitably within the range of from 1.5:1 to 4.5:1, preferably from 2.5:1 to 3.9:1. Suitably a dilute silicate solution or water glass is used which can have an SiO_2 content of from about 3 to about 12% by weight, preferably from about 5 to about 10% by weight. The silicate solution or water glass, which usually
35 has a pH around 13 or above 13, is acidified to a pH of from about 1 to about 4. The acidification can be carried out in known manner by addition of mineral acids, e.g.

5 sulphuric acid, hydrochloric acid and phosphoric acid, or optionally with other chemicals known as suitable for acidification of water glass, e.g. ammonium sulphate and carbon dioxide. When adding a mineral acid, the acidification is suitably carried out in two steps, a first step to a pH of about 8 to 9, whereupon a certain ripening, i.e., a particle growth, is allowed to occur before further acidification to a pH of from about 1 to about 4. However, it is preferred that the acidification is carried out by means of an acid cation exchanger which, among other things, lead to more stable products. The acidification is preferably carried out by means of a strongly acid cation exchange resin, for example of sulfonic acid type. It is preferred that the acidification is carried out to a pH of from about 2 to 4, most preferably from about 2.2 to 3.0. The product obtained, an acid sol or polysilicic acid, contains particles with a high specific surface area, normally above 1000 m²/g SiO₂ and usually around about 1300 to 1500 m²/g SiO₂.

The acid sol is then subjected to alkalisation, herein referred to as a first alkalisation step. The first alkalisation can be carried out by addition of conventional alkali, e.g. lithium hydroxide, sodium hydroxide, potassium hydroxide, ammonium hydroxide and mixtures thereof, and/or an aqueous silicate solution as defined above. Potassium and sodium water glass, particularly sodium water glass, with a molar ratio of SiO₂ to M₂O as defined above, is suitably used in the alkalisation step. The SiO₂ content of the water glass solutions used for the first alkalisation is suitably within the range of from about 3 to about 35% by weight and preferably within the range of from 5 to 30% by weight. The first alkalisation is suitably carried out to a pH of at least 6, usually at least 7 and preferably within the range of from 7.5 to 10.5. The first alkalisation is further suitably carried out to a final molar ratio of SiO₂ to M₂O, M being as defined above, of less than 100:1, suitably within the range of from about 20:1 to about 80:1, preferably from 30:1 to 70:1. In the preparation of a sol having a low S-value as defined above the degree of microgel can be influenced in several ways and be controlled to a desired value. The degree of microgel can be influenced by salt content, by adjustment of the concentration in the preparation of the acid sol and in the first alkalisation step since in this step the degree of microgel is influenced when the stability minimum for the sol is passed, at a pH of about 5. By prolonged times at this passage the degree of microgel can be directed to the desired value. It is particularly suitable to control the degree of microgel by adjustment of the dry content, the SiO₂ content, in the first alkalisation step whereby a higher dry content gives a lower S-value. By keeping the SiO₂ content in the first alkalisation step within the range of from 4.5 to 8% by weight the S-value can be controlled to the desired values of, for example, from 10 to 45%. To obtain sols with S-values within the range of from 20 to 40% the SiO₂ content in the first alkalisation step is

suitably kept within the range of from 5.0 to 7.5% by weight.

The alkalisol obtained in the first alka-
lisation step is then subjected to
particle growth so that particles with a lower specific surface area and higher stability are
obtained. The particle growth process should suitably be carried out to provide particles
5 with a specific surface area of at least 300 m²/g SiO₂, preferably at least 400 m²/g SiO₂,
and most preferably at least 550 m²/g SiO₂, and up to about 1200 m²/g SiO₂, suitably less
than 1000 m²/g SiO₂, notably up to 950 m²/g SiO₂. In a preferred embodiment of this
invention, the particle growth process is carried out to provide particles with a specific
surface area within the range of from 550 to 725 SiO₂, preferably from 575 to 700 m²/g
10 SiO₂. In another preferred embodiment of this invention, is carried out to provide particles
with a specific surface area of within the range of from 775 to 1200 m²/g SiO₂, preferably
from 800 to less than 1000 m²/g SiO₂. The decrease in surface area can be obtained by
storage at room temperature during somewhat longer times, a day up to about two days
and nights, or, preferably, by heat treatment. In the heat treatment, times and
15 temperatures can be adjusted so that shorter times are used at higher temperatures.
Even if it of course is possible to use fairly high temperatures during very short times it is,
from a practical point of view, more suitable to use lower temperatures during somewhat
longer times. In the heat treatment, the alkalisol should suitably be heated at a
temperature of at least 30°C, suitably from 35 to 95°C and preferably from 40 to 80°C.
20 The heat treatment should suitably be carried out for at least 10 minutes, suitably from 15
to 600 minutes and preferably from 20 to 240 minutes.

After the particle growth step, and optional cooling, the obtained silica sol is
again subjected to alka-
lisation, herein referred to as a second alka-
lisation step, which
further increases the pH. The second alka-
lisation can be carried out by addition of
25 conventional alkali, e.g. lithium hydroxide, sodium hydroxide, potassium hydroxide,
ammonium hydroxide and mixtures thereof, and/or an aqueous silicate solution as
defined above. Potassium and sodium water glass, particularly sodium water glass, with
a molar ratio of SiO₂ to M₂O as defined above, is suitably used in the second alka-
lisation step. The SiO₂ content of the water glass solutions used for the second alka-
lisation is
30 suitably within the range of from about 3 to about 35% by weight and preferably within
the range of from 5 to 30% by weight. The second alka-
lisation is suitably carried out to a
pH of at least 8.0, suitably at least 10.0, preferably at least 10.5 and most preferably at
least 10.6. The pH can be up to about 11.5, suitably up to 11.0. The second alka-
lisation
is further suitably carried out to a final molar ratio of SiO₂ to M₂O, M being as defined
35 above, within the range of from about 10:1 to 100:1 and suitably from 12:1 to 40:1,
preferably from 15:1 to 30:1.

In a preferred embodiment of the invention, the process also comprises concentration of the silica-based sol. Concentration can be carried out after the second alkalisation. Alternatively, or additionally, the alkalised sol obtained after the first alkalisation but before the particle growth or heat treatment step, or the sol obtained after the particle growth or heat treatment step but before the second alkalisation, can be subjected to concentration. Concentration can be carried out in known manner such as, for example, by osmotic methods, evaporation and ultrafiltration. The concentration is suitably carried out to produce silica contents of at least 10% by weight, preferably from 10 to 30% by weight, and more preferably from 12 to 25% by weight. The concentration is further suitably carried out so that the silica-based sol obtained in the process has a specific surface area of at least 80 m²/g aqueous sol, i.e., based on the weight of aqueous sol, preferably at least 85 m²/g aqueous sol, more preferably at least 90 m²/g aqueous sol and most preferably at least 95 m²/g aqueous sol. In a preferred embodiment of this invention, the specific surface area of the aqueous silica-based sols obtained is suitably at least 115 m²/g aqueous sol. Generally, the specific surface area of the aqueous sol obtained can be up to about 200 m²/g aqueous sol, suitably up to 150 m²/g aqueous sol, preferably up to 130 m²/g aqueous sol and most preferably up to 120 m²/g aqueous sol.

If desired, the silica-based sol can be modified by addition of compounds containing, for example, aluminium and/or boron. Suitable aluminium-containing compounds include aluminates like sodium aluminate and potassium aluminate, suitably sodium aluminate. The aluminium-containing compound is suitably used in the form of an aqueous solution. Suitable boron-containing compounds include boric acid, borates like sodium and potassium borate, suitably sodium borate, tetraborates like sodium and potassium tetraborate, suitably sodium tetraborate, and metaborates like sodium and potassium metaborate. The boron-containing compound is suitably used in the form of an aqueous solution.

When using an aluminium-containing compound in the process, it is suitable to add it to the sol subjected to particle growth or heat treatment, either before or after the second alkalisation step. Alternatively, or additionally, the aluminium-containing compound can be added to the silicate solution to be acidified, to the acid sol or to the alkalised sol obtained in the first alkalisation step before the particle growth or heat treatment step. The aluminium-containing compound can be added in admixture with acid in the acidification step and in admixture with alkali or silicate solution in any of the alkalisation steps. The aluminium-containing compound is suitably added in an amount such that the obtained sol has a molar ratio of Al₂O₃ to SiO₂ as defined above,

When using a boron-containing compound in the process, it is suitable to add it

to the sol subjected to particle growth or heat treatment, either before or after the second alkalisation step. Alternatively, or additionally, the boron-containing compound can be added to the silicate solution to be acidified, to the acid sol or to the alkalised sol obtained in the first alkalisation step before the particle growth or heat treatment step.

- 5 The boron-containing compound can be added in admixture with acid in the acidification step and in admixture with alkali or silicate solution in any of the alkalisation steps. The boron-containing compound is suitably added in an amount such that the obtained sol has a molar ratio of B to SiO_2 as defined above. If both aluminium-containing and boron-containing compounds are used, they are suitably added in amounts such that the
10 obtained sol has a molar ratio of Al to B suitably as defined above.

If the sol, before any aluminium and/or boron modification, contains too high amounts of alkali metal ions or ammonium ions, it is preferable to remove at least part of these ions, for example by ion exchange, to provide silica-based sols with a final molar ratio of SiO_2 to M_2O within the desired range as defined above.

- 15 According to the present process, silica-based sols, notably stable silica-based sols, having the above characteristics can be prepared and the produced sols exhibit good storage stability and can be stored for several months without any substantial decrease of the specific surface area and without gelation.

- The silica-based sols of this invention are suitable for use as flocculating agents,
20 for example in the production of pulp and paper, notably as drainage and retention aids, and within the field of water purification, both for purification of different kinds of waste water and for purification specifically of white water from the pulp and paper industry. The silica-based sols can be used as flocculating agents, notably as drainage and retention aids, in combination with organic polymers which can be selected from anionic, amphoteric,
25 non-ionic and cationic polymers and mixtures thereof, herein also referred to as "main polymer". The use of such polymers as flocculating agents and as drainage and retention aids is well known in the art. The polymers can be derived from natural or synthetic sources, and they can be linear, branched or cross-linked. Examples of generally suitable main polymers include anionic, amphoteric and cationic starches, anionic, amphoteric and
30 cationic guar gums, and anionic, amphoteric and cationic acrylamide-based polymers, as well as cationic poly(diallyldimethyl ammonium chloride), cationic polyethylene imines, cationic polyamines, polyamidoamines and vinylamide-based polymers, melamine-formaldehyde and urea-formaldehyde resins. Suitably the silica-based sols are used in combination with at least one cationic or amphoteric polymer, preferably cationic polymer.
35 Cationic starch and cationic polyacrylamide are particularly preferred polymers and they can be used singly, together with each other or together with other polymers, e.g. other

cationic polymers or anionic polyacrylamide. The molecular weight of the main polymer is suitably above 1,000,000 and preferably above 2,000,000. The upper limit is not critical; it can be about 50,000,000, usually 30,000,000 and suitably about 25,000,000. However, the molecular weight of polymers derived from natural sources may be higher.

5 When using the silica-based sols in combination with main polymer(s) as mentioned above, it is further preferred to use at least one low molecular weight (hereinafter LMW) cationic organic polymer, commonly referred to and used as anionic trash catchers (ATC). ATC's are known in the art as neutralizing and/or fixing agents for detrimental anionic substances present in the stock and the use thereof in combination with
10 drainage and retention aids often provide further improvements in drainage and/or retention. The LMW cationic organic polymer can be derived from natural or synthetic sources, and preferably it is an LMW synthetic polymer. Suitable organic polymers of this type include LMW highly charged cationic organic polymers such as polyamines, polyamideamines, polyethyleneimines, homo- and copolymers based on diallyldimethyl
15 ammonium chloride, (meth)acrylamides and (meth)acrylates. In relation to the molecular weight of the main polymer, the molecular weight of the LMW cationic organic polymer is preferably lower; it is suitably at least 1,000 and preferably at least 10,000. The upper limit of the molecular weight is usually about 700,000, suitably about 500,000 and usually about 200,000. Preferred combinations of polymers that can be co-used with the silica-based sols
20 of this invention include LMW cationic organic polymer in combination with main polymer(s), such as, for example, cationic starch and/or cationic polyacrylamide, anionic polyacrylamide as well as cationic starch and/or cationic polyacrylamide in combination with anionic polyacrylamide.

 The components of the drainage and retention aids according to the invention
25 can be added to the stock in conventional manner and in any order. When using drainage and retention aids comprising a silica-based sol and an organic polymer, e.g. a main polymer, it is preferred to add the polymer to the stock before adding the silica-based sol, even if the opposite order of addition may be used. It is further preferred to add the main polymer before a shear stage, which can be selected from pumping,
30 mixing, cleaning, etc., and to add the silica-based sol after that shear stage. LMW cationic organic polymers, when used, are preferably introduced into the stock prior to introducing the main polymer. Alternatively, the LMW cationic organic polymer and the main polymer can be introduced into stock essentially simultaneously, either separately or in admixture, for example as disclosed in U.S. Patent No. 5,858,174, which is hereby
35 incorporated herein by reference. The LMW cationic organic polymer and the main polymer are preferably introduced into the stock prior to introducing the silica-based sol.

In a preferred embodiment of this invention, the silica-based sols are used as drainage and retention aids in combination with at least one organic polymer, as described above, and at least one aluminium compound. Aluminium compounds can be used to further improve the drainage and/or retention performance of stock additives comprising silica-based sols. Suitable aluminium salts include alum, aluminates, aluminium chloride, aluminium nitrate and polyaluminium compounds, such as polyaluminium chlorides, polyaluminium sulphates, polyaluminium compounds containing both chloride and sulphate ions, polyaluminium silicate-sulphates, and mixtures thereof. The polyaluminium compounds may also contain other anions, for example anions from phosphoric acid, organic acids such as citric acid and oxalic acid. Preferred aluminium salts include sodium aluminate, alum and polyaluminium compounds. The aluminium compound can be added before or after the addition of the silica-based sol. Alternatively, or additionally, the aluminium compound can be added simultaneously with the silica-based sol at essentially the same point, either separately or in admixture with it, for example as disclosed by U.S. Patent No 5,846,384 which is hereby incorporated herein by reference. In many cases, it is often suitable to add an aluminium compound to the stock early in the process, for example prior to the other additives.

The components of the drainage and retention aids according to the invention are added to the stock to be dewatered in amounts which can vary within wide limits depending on, inter alia, type and number of components, type of furnish, filler content, type of filler, point of addition, etc. Generally the components are added in an amount that give better drainage and/or retention than is obtained when not adding the components. The silica-based sol is usually added in an amount of at least 0.001% by weight, often at least 0.005% by weight, calculated as SiO_2 and based on dry stock substance, i.e. cellulosic fibres and optional fillers, and the upper limit is usually 1.0% and suitably 0.5% by weight. The main polymer is usually added in an amount of at least 0.001%, often at least 0.005% by weight, based on dry stock substance, and the upper limit is usually 3% and suitably 1.5% by weight. When using an LMW cationic organic polymer in the process, it can be added in an amount of at least 0.05%, based on dry substance of the stock to be dewatered. Suitably, the amount is in the range of from 0.07 to 0.5%, preferably in the range from 0.1 to 0.35%. When using an aluminium compound in the process, the total amount introduced into the stock to be dewatered depends on the type of aluminium compound used and on other effects desired from it. It is for instance well known in the art to utilise aluminium compounds as precipitants for rosin-based sizing agents. The total amount added is usually at least 0.05%, calculated as Al_2O_3 and based on dry stock substance. Suitably the amount is in the range of from 0.1 to 3.0%, preferably in the range

from 0.5 to 2.0%.

Further additives which are conventional in papermaking can of course be used in combination with the additives according to the invention, such as, for example, dry strength agents, wet strength agents, optical brightening agents, dyes, sizing agents like
5 rosin-based sizing agents and cellulose-reactive sizing agents, e.g. alkyl and alkenyl ketene dimers and ketene multimers, alkyl and alkenyl succinic anhydrides, etc. The cellulosic suspension, or stock, can also contain mineral fillers of conventional types such as, for example, kaolin, china clay, titanium dioxide, gypsum, talc and natural and synthetic calcium carbonates such as chalk, ground marble and precipitated calcium carbonate.

10 The process of this invention is used for the production of paper. The term "paper", as used herein, of course include not only paper and the production thereof, but also other cellulosic fibre-containing sheet or web-like products, such as for example board and paperboard, and the production thereof. The process can be used in the production of paper from different types of suspensions of cellulose-containing fibres and the
15 suspensions should suitably contain at least 25% by weight and preferably at least 50% by weight of such fibres, based on dry substance. The suspension can be based on fibres from chemical pulp such as sulphate, sulphite and organosolv pulps, mechanical pulp such as thermomechanical pulp, chemo-thermomechanical pulp, refiner pulp and groundwood pulp, from both hardwood and softwood, and can also be based on recycled fibres,
20 optionally from de-inked pulps, and mixtures thereof. The pH of the suspension, the stock, can be within the range of from about 3 to about 10. The pH is suitably above 3.5 and preferably within the range of from 4 to 9.

The invention is further illustrated in the following Examples which, however, are not intended to limit the same. Parts and % relate to parts by weight and % by weight,
25 respectively, unless otherwise stated.

Example 1

A standard silica sol was prepared as follows:

762.7 g sodium water glass with a molar ratio of SiO_2 to Na_2O of 3.3 and SiO_2
30 content of 27.1% was diluted with water to 3000 g yielding a silicate solution (I) with a SiO_2 content of 6.9% by weight. 2800 g of this silicate or water glass solution was passed through a column filled with a strong cation exchange resin saturated with hydrogen ions. 2450 g of ion-exchanged water glass or polysilicic acid (II) with an SiO_2 content of 6.5%
by weight and a pH of 2.4 was collected from the ion exchanger. 1988 g of the polysilicic
35 acid (II) was fed into a reactor and diluted with 12.3 g water. 173.9 g of the 6.9% silicate solution (I) was then added under vigorous agitation. The resulting solution was then

12

heated at 85°C for 60 minutes and then cooled to 20°C. The obtained silica sol (1a) had the following characteristics:

Sol 1a (ref.): SiO₂ content = 7.3% by weight, molar ratio SiO₂/Na₂O = 40, pH = 10.2,

S-value = 29%, viscosity = 2.2 cP, specific surface areas = 530 m²/g SiO₂

5

and 39 m²/g aqueous sol.

Two further silica sols, Sol 1b and Sol 1c, were produced which had the following characteristics:

Sol 1b (ref.): SiO₂ content = 7.3% by weight, molar ratio SiO₂/Na₂O = 63, pH = 10.0,

S-value = 26%, viscosity = 2.7 cP, specific surface areas = 500 m²/g SiO₂

10

and 36.5 m²/g aqueous sol

Sol 1c (ref.): SiO₂ content = 5.4% by weight, molar ratio SiO₂/Na₂O = 35, pH = 9.8,

S-value = 32%, viscosity = 1.6 cP, specific surface areas = 690 m²/g SiO₂

and 37 m²/g aqueous sol

15

Example 2

Six silica-based sols according to the invention was prepared from a polysilicic acid similar to the polysilicic acid (II) produced with the same ion exchange process and with an SiO₂ content of 5.46% by weight. To 102.0 kg of the polysilicic acid was added 1.46 kg of sodium water glass with a ratio SiO₂/Na₂O of 3.3 under vigorous agitation 20 resulting in a solution with a molar ratio SiO₂/Na₂O of 54.0. This solution was heat treated at 60°C for 2 h 20 min and cooled to 20°C whereupon the product was concentrated to a SiO₂ content of 15.6% by weight. This intermediate sol product was now divided into six separate samples, a to f. Samples a to c were further alkalisied with NaOH, samples d to f with water glass, to achieve sols with a molar ratio SiO₂/Na₂O between 21.5 and 34.0 25 and a silica content of about 15.0% by weight. The obtained silica-based sols had the characteristics set forth in Table 1:

Table 1

30	Sol	Molar ratio [SiO ₂ /Na ₂ O]	pH	S-value [%]	Viscosity [cp]	Specific Surface Areas	
						[m ² /g SiO ₂]	[m ² /g aq. sol]
	Sol 2a	21.5	10.7	31	17	720	108.0
	Sol 2b	28.0	10.3	30	29	710	106.5
	Sol 2c	34.0	10.0	29	40	690	103.5
	Sol 2d	21.5	10.7	31	20	680	102.0
35	Sol 2e	28.0	10.3	29	34	670	100.5
	Sol 2f	33.0	10.0	29	38	680	102.0

Example 3

A polysilicic acid (II) produced with the above ion exchange process and alkalis with water glass to a molar ratio $\text{SiO}_2/\text{Na}_2\text{O}$ of 54.0 as in Example 2 was heat treated at 60°C for 1 h. To 58 kg of this product was added 7.25 kg of diluted water glass with a molar ratio $\text{SiO}_2/\text{Na}_2\text{O}$ of 3.3 and silica content 5.5% by weight. The resulting silica-based sol, Sol 3, was concentrated to a silica content of 15.2% by weight and had a molar ratio $\text{SiO}_2/\text{Na}_2\text{O} = 24$, pH = 10.7, S-value = 34, viscosity = 9.0 cp and specific surface areas = 760 m²/g SiO_2 and 115.5 m²/g aqueous sol.

10

Example 4

1000 g polysilicic acid (II) with an SiO_2 content of 5.5% by weight was mixed with 14.5 g water glass solution with an SiO_2 content of 27.1% by weight and a molar ratio $\text{SiO}_2/\text{Na}_2\text{O} = 3.3$ under vigorous agitation resulting in a product with a molar ratio $\text{SiO}_2/\text{Na}_2\text{O}$ of 51 and a silica content of 5.8% by weight SiO_2 , which was heat treated at 60°C for 1.5 h and then concentrated to a silica content of 16.7% by weight SiO_2 . 283 g of the product obtained was mixed with 33.0 g NaOH resulting in a silica sol, Sol 4, with SiO_2 content = 15.2% by weight, molar ratio $\text{SiO}_2/\text{Na}_2\text{O} = 21$, pH = 10.6, S-value = 32%, viscosity = 14.2 cP and specific surface areas = 720 m²/g SiO_2 and 109.4 m²/g aqueous sol.

20

Example 5

Drainage performance was evaluated by means of a Dynamic Drainage Analyser (DDA), available from Akribi, Sweden, which measures the time for draining a set volume of stock through a wire when removing a plug and applying vacuum to that side of the wire opposite to the side on which the stock is present.

25

The stock used was based on a blend of 60% bleached birch sulphate and 40% bleached pine sulphate to which was added 30% ground calcium carbonate as a filler. Stock volume was 800 ml, consistency 0.25 % and pH about 8.0. Conductivity of the stock was adjusted to 0.47 mS/cm by addition of sodium sulphate.

30

In the tests, the silica-based sols were used in conjunction with a cationic polymer, Raisamyl 142, which is a conventional medium-high cationised starch having a degree of substitution of 0.042, which was added to the stock in an amount of 12 kg/tonne, calculated as dry starch on dry stock system. Silica-based sols according to Examples 1 to 4 were tested in this Example. In addition, Sols 5 and 6 were also tested for comparison purposes. Sol 5 is a commercial silica sol with an S-value = 45%, SiO_2 content = 15.0% by weight, molar ratio $\text{SiO}_2/\text{Na}_2\text{O} = 40$, viscosity = 3.0 cP, specific surface areas = 500

35

14

m^2/g SiO_2 and $75 \text{ m}^2/\text{g}$ aqueous sol. Sol 6 is another commercial silica sol with an S-value = 36%, SiO_2 content = 10.0% by weight, molar ratio $\text{SiO}_2/\text{Na}_2\text{O} = 10$, viscosity = 2.5 cP, specific surface areas = $880 \text{ m}^2/\text{g}$ SiO_2 and $88 \text{ m}^2/\text{g}$ aqueous sol. The silica-based sols were added in an amount of 0.5 kg/ton, calculated as SiO_2 and based on dry stock

5 system.

The stock was stirred in a baffled jar at a speed of 1500 rpm throughout the test and chemical additions were conducted as follows: i) adding cationic starch to the stock following by stirring for 30 seconds, ii) adding silica-based sol to the stock followed by stirring for 15 seconds, iii) draining the stock while automatically recording the drainage

10 time.

Drainage times for the different silica sols are shown in Table 2:

Table 2

Silica sol		Dewatering time
		[sec]
15	Sol 1a (ref.)	12.0
	Sol 1b (ref.)	11.1
	Sol 1c (ref.)	12.0
	Sol 2a	9.8
	Sol 2d	9.7
20	Sol 3	9.5
	Sol 4	9.4
	Sol 5 (ref.)	12.0
	Sol 6 (ref.)	9.8

15

Claims

1. Process for the production of paper which comprises:

- (a) providing an aqueous suspension containing cellulosic fibres, and optional fillers;
- (b) providing an aqueous silica-based sol having a specific surface area of at least
5 90 square meters per gram of aqueous sol (m^2/g aqueous sol) and containing
silica-based particles with a specific surface area less than 1000 square meters
per gram of silica (m^2/g SiO_2);
- (c) optionally diluting the aqueous silica-based sol with water;
- (d) adding to the suspension at least one charged organic polymer and the aqueous
10 silica-based sol according to (b) or (c);
- (e) forming and draining the obtained suspension on a wire.

2. Process for the production of paper which comprises:

- (a) providing an aqueous suspension containing cellulosic fibres, and optional fillers;
- (b) providing an aqueous silica-based sol having a specific surface area of at least
15 90 square meters per gram of aqueous sol (m^2/g aqueous sol) and an S-value
within the range of from 10 to 45%;
- (c) optionally diluting the aqueous silica-based sol with water;
- (d) adding to the suspension at least one charged organic polymer and the aqueous
silica-based sol according to (b) or (c);
- 20 (e) forming and draining the obtained suspension on a wire.

3. Process according to claim 1 or 2, c h a r a c t e r i s e d in that the silica-based sol has a molar ratio of SiO_2 to M_2O , where M is alkali metal ion and/or ammonium, within the range of from 15:1 to 40:1.

4. Process according to claim 1, 2 or 3, c h a r a c t e r i s e d in that the sol
25 contains silica-based particles having a specific surface area of at least $550 \text{ m}^2/\text{g}$ SiO_2 .

5. Process according to any of the preceding claims, c h a r a c t e r i s e d in that the sol has a specific surface area in the range of from 95 to $130 \text{ m}^2/\text{g}$ aqueous sol.

6. Process according to any of the preceding claims, c h a r a c t e r i s e d
30 in that the charged organic polymer is cationic starch or cationic polyacrylamide.

7. Aqueous silica-based sol, c h a r a c t e r i s e d in that it has a specific surface area of at least 115 square meters per gram of aqueous sol (m^2/g aqueous sol) and contains silica-based particles with a specific surface area of less than 1000 square meters per gram of silica (m^2/g SiO_2).

35 8. Aqueous silica-based sol, c h a r a c t e r i s e d in that it has a specific surface area of at least 115 square meters per gram of aqueous sol (m^2/g aqueous sol)

and an S-value within the range of from 10 to 45%.

9. Aqueous silica-based sol according to claim 7 or 8, characterised in that it has a molar ratio of SiO_2 to M_2O , where M is alkali metal or ammonium, within the range of from 15:1 to 40:1.

5 10. Aqueous silica-based sol according to claim 7, 8 or 9, characterised in that it contains silica-based particles having a specific surface area of at least $550 \text{ m}^2/\text{g SiO}_2$.

11. Aqueous silica-based sol according to claim 7, 8, 9 or 10, characterised in that it has an S-value within the range of from 25 to 35%.

10 12. Aqueous silica-based sol according to any of claims 7 to 11, characterised in that it has a silica content of at least 10% by weight.

13. Process for the production of a silica-based sol which comprises:

- (a) acidifying an aqueous silicate solution to a pH of from 1 to 4 to form an acid sol;
(b) alkalising the acid sol at an SiO_2 content within the range of from 4.5 to 8% by weight
15 to a pH of at least 7;
(c) allowing particle growth of the alkalised sol for at least 10 minutes;
(d) alkalising the obtained sol to a pH of at least 10.0; and
(e) optionally concentrating the sol obtained according to (b), (c) or (d) to provide a silica-based sol having a specific surface area of at least 90 square meters per gram of
20 aqueous sol ($\text{m}^2/\text{g aqueous sol}$).

14. Process for the production of a silica-based sol which comprises:

- (a) acidifying an aqueous silicate solution to a pH of from 1 to 4 to form an acid sol;
(b) alkalising the acid sol at an SiO_2 content within the range of from 4.5 to 8% by weight;
(c) heat-treating the alkalised sol at a temperature of at least 30°C ;
25 (d) alkalising the heat-treated sol to a pH of at least 10.0; and
(e) optionally concentrating the sol obtained according to (b), (c) or (d) to provide a silica-based sol having a specific surface area of at least 90 square meters per gram of
aqueous sol ($\text{m}^2/\text{g aqueous sol}$).

30 15. Process according to claim 13 or 14, characterised in that it comprises (e) concentrating the sol obtained according to (c) or (d) to provide a silica-based sol having a specific surface area of at least 95 square meters per gram of aqueous sol ($\text{m}^2/\text{g aqueous sol}$).

35 16. Process according to claim 13, 14 or 15, characterised in that the alkalisation according to (b) and (d) is carried out by means of an aqueous silicate solution.

17. Process according to any of claims 13 to 16, characterised in

17

that the particle growth and heat-treatment according to (c) is carried out at a temperature within the range of from 35 to 95°C.

18. Process according to any of claims 13 to 17, characterised in that the particle growth and heat-treatment according to (c) is carried out for 20 to 240 minutes.

19. Process according to any of claims 13 to 18, characterised in that the alkalisation according to (d) produces a silica-based sol having a molar ratio of SiO_2 to M_2O , where M is alkali metal or ammonium, within the range of from 15:1 to 30:1 and a pH of at least 10.6.

20. Process according to any of claims 13 to 19, characterised in that it further comprises addition of an aluminium-containing compound and/or a boron-containing compound.

21. Aqueous silica-based sol obtainable by a process according to any of claims 13 to 20.

22. Use of a silica-based sol according to any of claims 7 to 12 or 21 or produced by a process according to any of claims 13 to 20 as a drainage and retention aid in the production of paper.

Abstract

The invention relates to a process for the production of paper which comprises (a) providing an aqueous suspension containing cellulosic fibres, and optional fillers; (b) providing an aqueous silica-based sol; (c) optionally diluting the aqueous silica-based sol with water; (d) adding to the suspension at least one charged organic polymer and the aqueous silica-based sol according to (b) or (c); (e) forming and draining the obtained suspension on a wire. The sol according to (a) has a specific surface area of at least 90 square meters per gram of aqueous sol and contains silica-based particles with a specific surface area less than 1000 square meters per gram of silica; or has a specific surface area of at least 90 square meters per gram of aqueous sol and an S-value within the range of from 10 to 45%.

The invention further relates to an aqueous silica-based sol having a specific surface area of at least 115 square meters per gram of aqueous sol and contains silica-based particles with a specific surface area of less than 1000 square meters per gram of silica. The invention also relates to an aqueous silica-based sol having a specific surface area of at least 115 square meters per gram of aqueous sol and an S-value within the range of from 10 to 45%.

The invention also relates to a process for the production of a silica-based sol which comprises (a) acidifying an aqueous silicate solution to a pH of from 1 to 4 to form an acid sol; (b) alkalising the acid sol at an SiO_2 content within the range of from 4.5 to 8% by weight to a pH of at least 7; (c) allowing particle growth of the alkalised sol for at least 10 minutes; (d) alkalising the obtained sol to a pH of at least 10.0; and (e) optionally concentrating the sol obtained according to (b), (c) or (d) to provide a silica-based sol having a specific surface area of at least 90 square meters per gram of aqueous sol. The invention further relates to a process for the production of a silica-based sol which comprises (a) acidifying an aqueous silicate solution to a pH of from 1 to 4 to form an acid sol; (b) alkalising the acid sol at an SiO_2 content within the range of from 4.5 to 8% by weight; (c) heat-treating the alkalised sol at a temperature of at least 30°C; (d) alkalising the heat-treated sol to a pH of at least 10.0; and (e) optionally concentrating the sol obtained according to (b), (c) or (d) to provide a silica-based sol having a specific surface area of at least 90 square meters per gram of aqueous sol. The invention also relates to an aqueous silica-based sol obtainable by the process and the use of the silica-based sol as a drainage and retention aid in the production of paper.

